Supplementary information

A NHC silver(I) macrometallocycle: synthesis, structure and selective recognition of iodide anion

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1. CCDC numbers for complex 1

CCDC 853182 contains the supplementary crystallographic data for complex **1**. These data can be obtained free of charge via http//www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

2. The Fig.s of fluorescence and UV/vis spectroscopies for complex 1 (Fig. S1-Fig. S4).

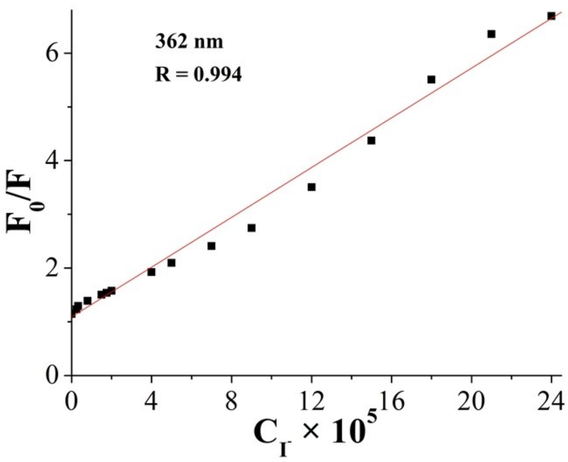

Fig. S1 Stern-Volmer plot of **1** quenched by I^- in acetonitrile solutions at 25 ˚C. K_{SV} was calculated as 2.3×10^4 M^{-1} (R = 0.994).

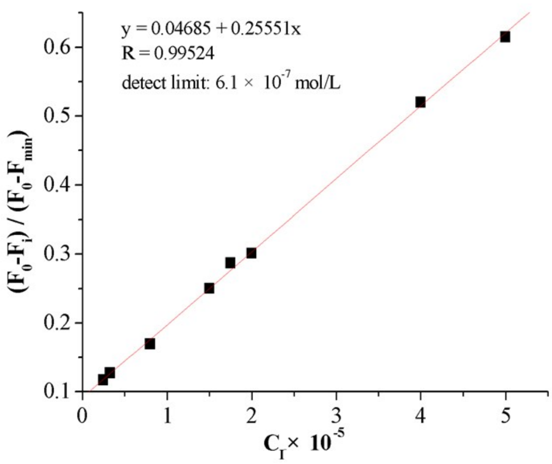

Fig. S2 Emission (at 362 nm) of **1** at different concentrations of I^- (0, 0.25, 0.33, 0.8, 1.5, 1.75, 2.0, 4.0, 5.0 × 10^{-5} mol/L) added, normalized between the minimum emission (0.0 mol/L I^-) and the emission at 5.0× 10^{-5} mol/L I^- in CH_3CN at 25 ˚C. The detection limit was determined to be 6.1 × 10^{-7} mol/L.

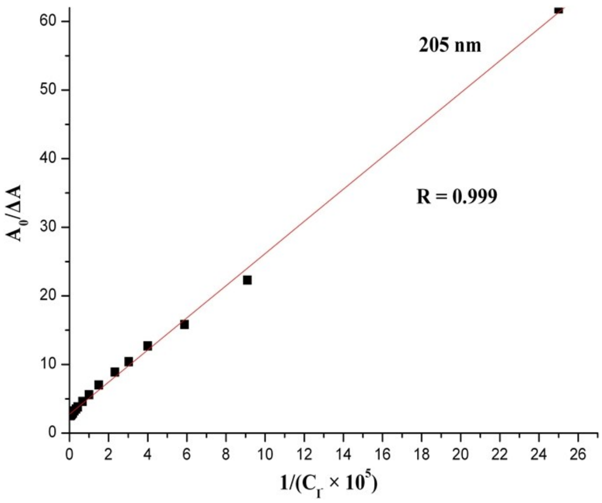

Fig. S3 Benesi-Hildebrand plot of **1** (1 × 10^{-5} mol/L) in the presence of I^- in acetonitrile at 205 nm at 25 ˚C. C_{I^-} is 0, 0.04, 0.11, 0.17, 0.25, 0.33, 0.43, 0.67, 1.0, 1.5, 2.4, 3.0, 4.0, 6.0, 9.0, 12.0, 15.0, 20.0 × 10^{-5} mol/L.

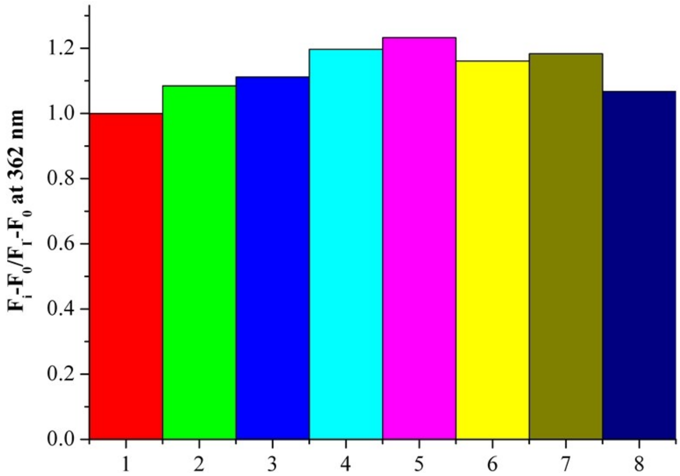

Fig. S4 Change ratio $((F_i-F_0)/(F_I-F_0))$ of fluorescence intensity of **1** upon addition of 1 equiv. I^- in the presence of 5 equiv. background anions. 1: I^-; 2: I^- + F^-; 3: I^- + Cl^-; 4: I^- + Br^-; 5: I^- + $H_2PO_4^-$; 6: I^- + HSO_4^-; 7: I^- + OAc^-; 8: I^- + NO_3^- in acetonitrile at 25˚C. F_i is the fluorescence intensity in the presence of I^- and other anions. F_{I^-} is the fluorescence intensity in the presence of I^- alone.

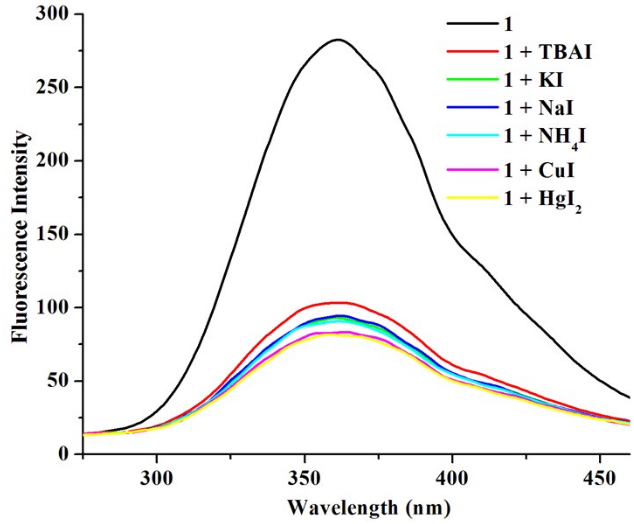

Fig. S5 Fluorescence spectra of **1** (1×10^{-5}mol/L) with I^- salts with different countercations (TBA^+, K^+, Na^+, NH_4^+, Cu^+, Hg^{2+}).

3. Whole ^1H NMR spectra for Complex 1 and $1\cdot I^-$

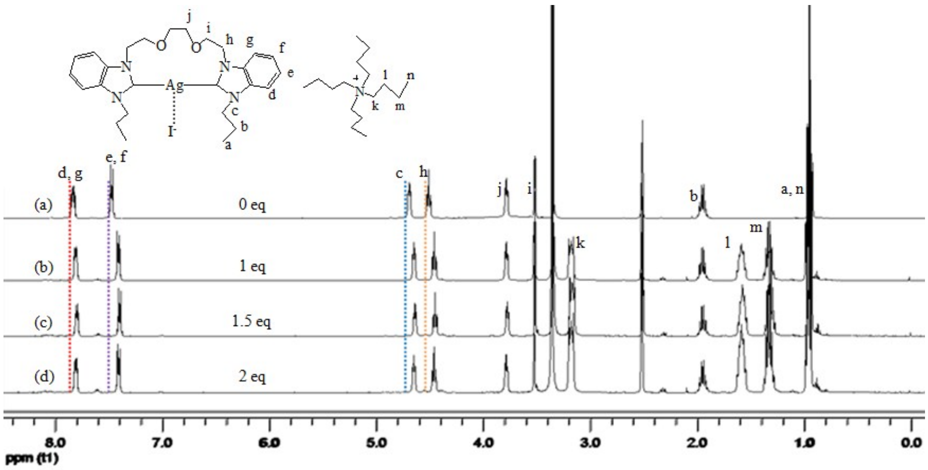

Fig. S6 Whole ^1H NMR spectra in DMSO-d_6. (a) Complex **1**; (b) **1** and 1 equiv. of TBAI; (c) **1** and 1.5 equiv of TBAI; (d) **1** and 2 equiv. of TBAI.

4. HRMS spectrum of 1·I⁻.

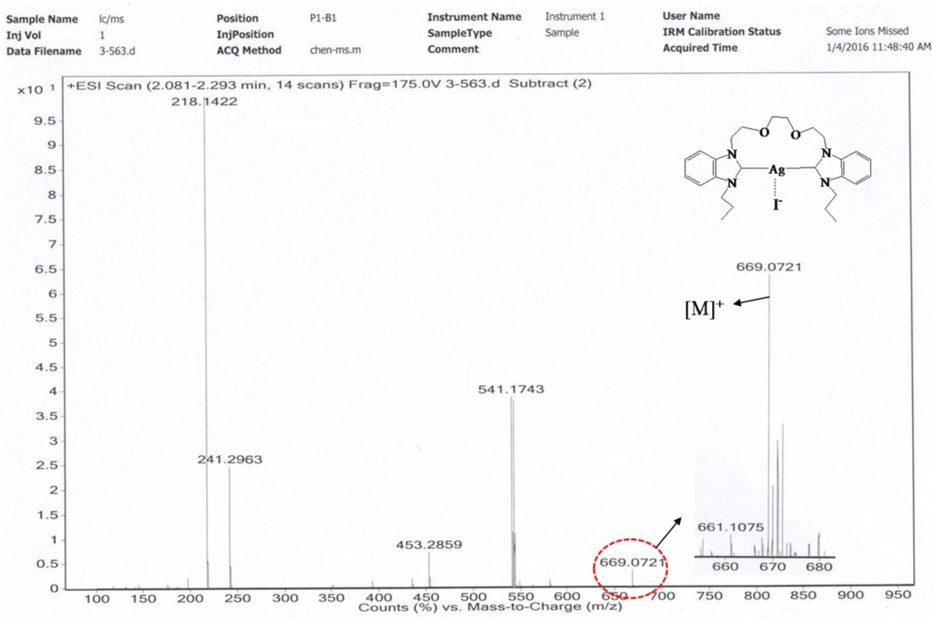

Fig. S7 HRMS spectrum of **1·I⁻**. MS (EI): m/z $[M]^+$ = 669.0721.

5. The infrared spectra of complex 1 and 1·I⁻

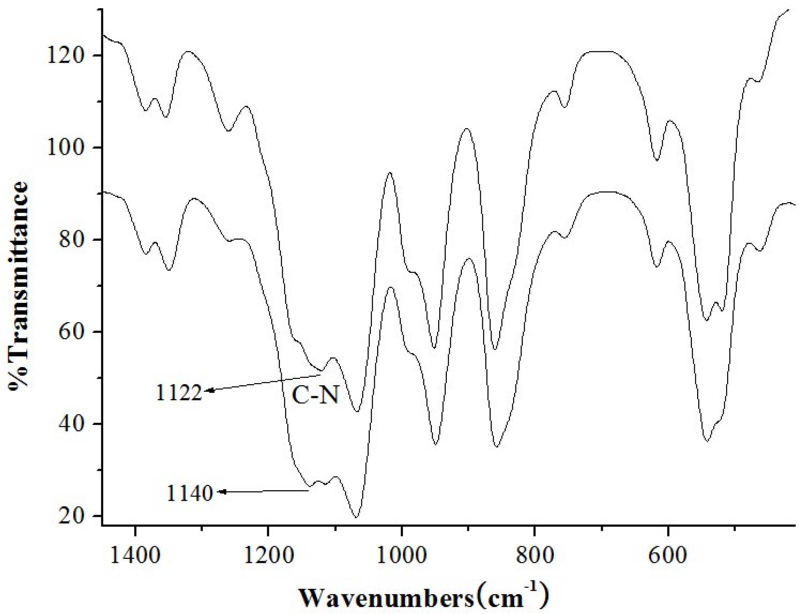

Fig. S8 Infrared spectroscopy of complex **1** (top) and **1**·I⁻ (bottom).

6. The ^{1}H NMR and ^{13}C NMR spectra of precursor and complex 1.

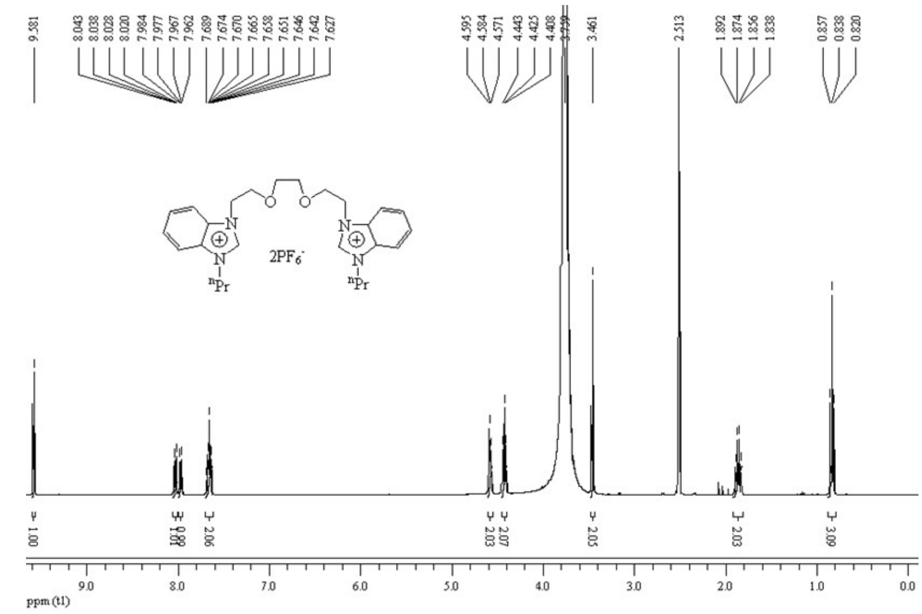

Fig. S9 ^{1}H NMR of 1,1'-[1,2-ethanediyl-bis(oxy-1,2-ethanediyl)]-bis(3-^{n}propylbenzimidazolium-1-yl) dihexafluorophosphate (**$LH_2\cdot(PF_6)_2$**) (400 MHz, DMSO-d_6).

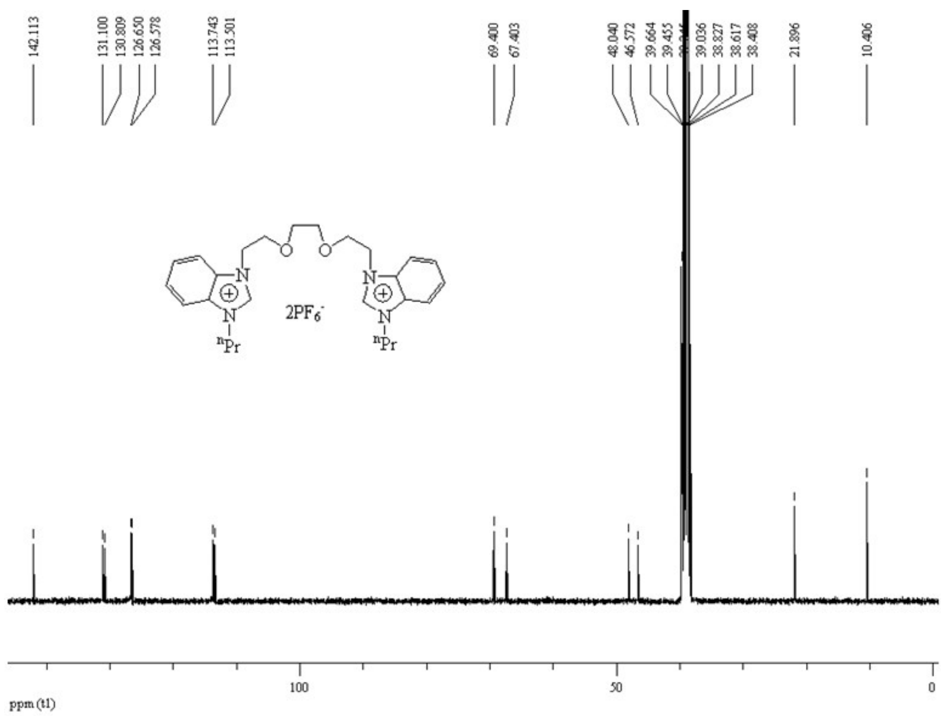

Fig. S10 ^{13}C NMR of 1,1'-[1,2-ethanediyl-bis(oxy-1,2-ethanediyl)]-bis(3-^{n}propylbenzimidazolium-1-yl) dihexafluorophosphate (**$LH_2\cdot(PF_6)_2$**) (100 MHz, DMSO-d_6).

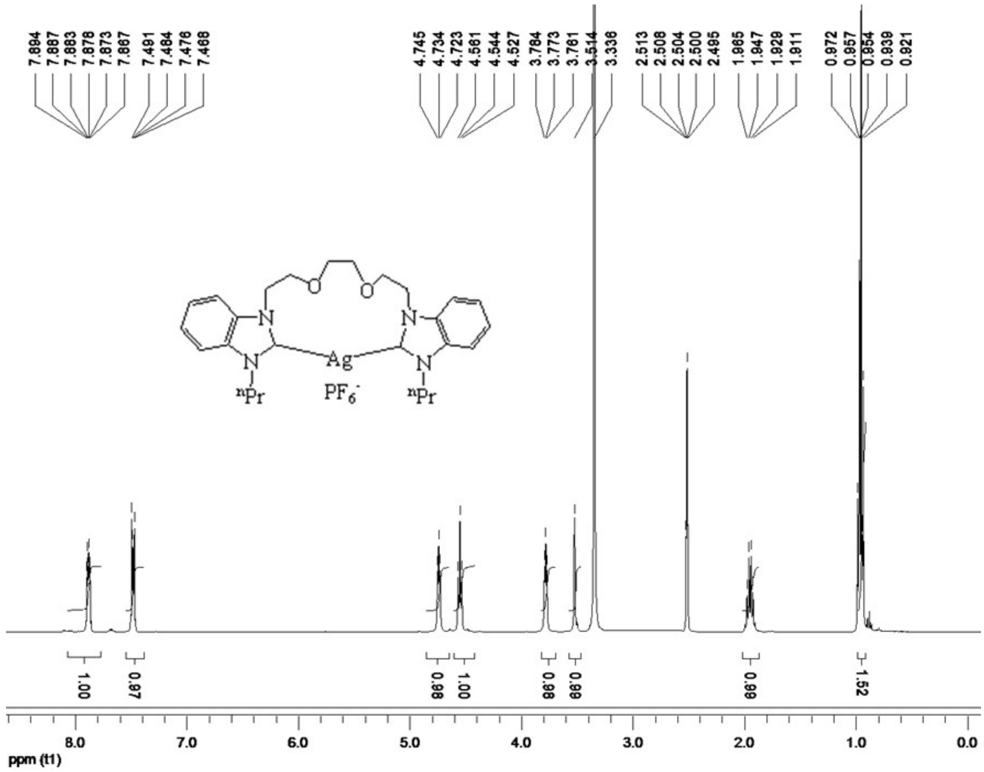

Fig. S11 [1]H NMR of Silver-{C,C'-1,1'-[1,2-ethanediyl-bis(oxy-1,2-ethanediyl)]-bis(3-^{n}propyl-benzimidazolium-1-yl)} hexafluorophosphate (**1**) (400 $MH_{Z,}$ DMSO-d_6).

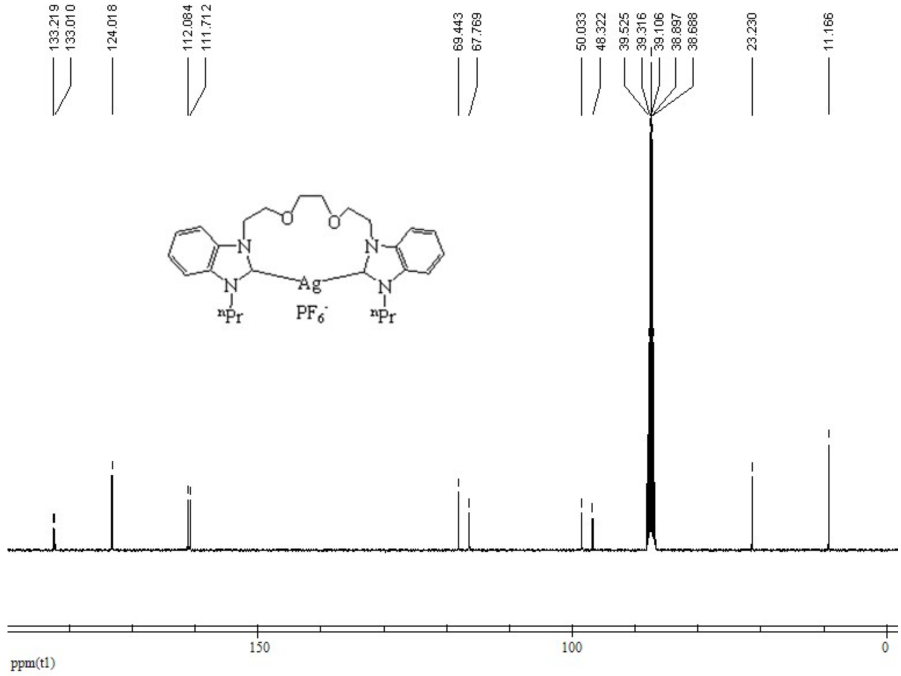

Fig. S12 [13]C NMR of Silver-{C,C'-1,1'-[1,2-ethanediyl-bis(oxy-1,2-ethanediyl)]-bis(3-^{n}propyl-benzimidazolium-1-yl)} hexafluorophosphate (**1**) (100 $MH_{Z,}$ DMSO-d_6).

7. HRMS spectra of $LH_2{\cdot}I_2$, $LH_2{\cdot}(PF_6)_2$ and 1.

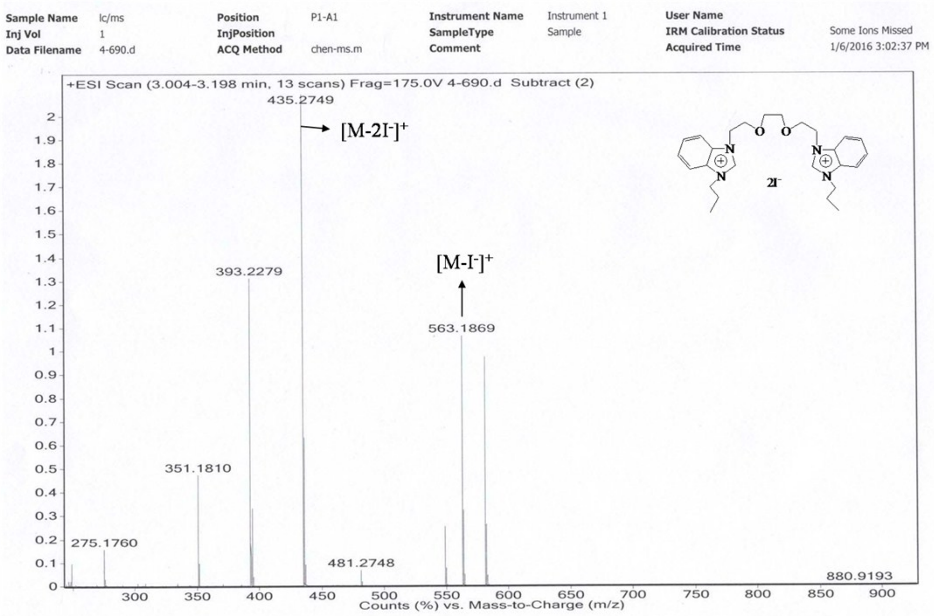

Fig. S13 HRMS spectrum of $\mathbf{LH_2{\cdot}I_2}$. MS (EI): m/z $[M\text{-}I^-]^+$ = 563.1869, m/z $[M\text{-}2I^-]^+$ = 435.2749.

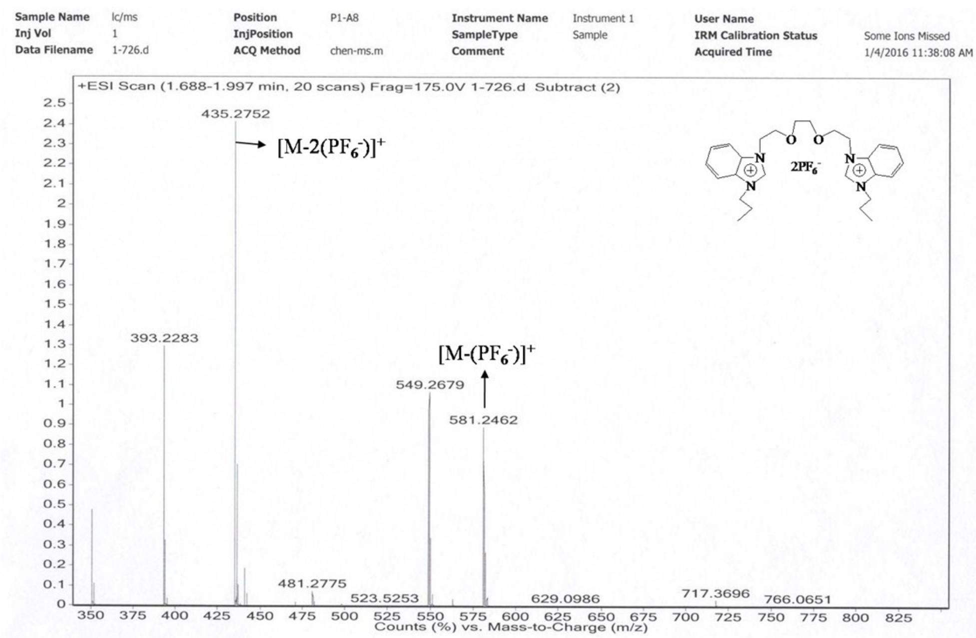

Fig. S14 HRMS spectrum of $\mathbf{LH_2{\cdot}(PF_6)_2}$. MS (EI): m/z $[M\text{-}(PF_6^-)]^+$ = 581.2462, m/z $[M\text{-}2(PF_6^-)]^+$ = 435.2752.

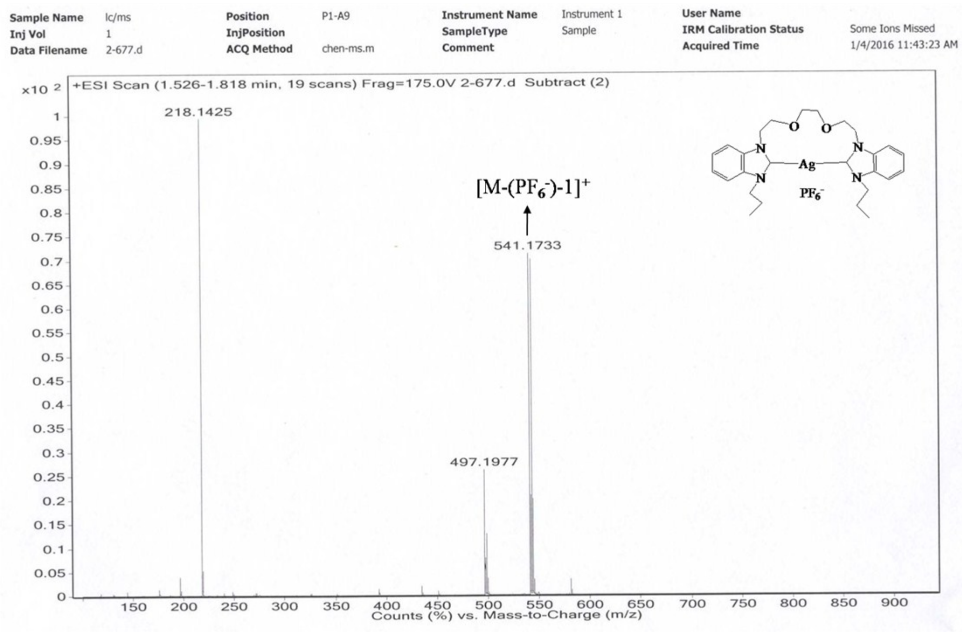

Fig. S15 HRMS spectrum of **1**. MS (EI): m/z [M-(PF_6^-)-1]$^+$ = 541.1733.